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INFLUENCE OF HUMIC ACID ON MIGRATION OF
^{60}Co, ^{85}Sr AND ^{137}Cs IN COASTAL SANDY SOIL

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Influence of Humic Acid on Migration of ^{60}Co, ^{85}Sr and ^{137}Cs in Coastal Sandy Soil

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Sorption and migration experiments were performed by both batch and column methods, to study influence of humic acid complexing on the mobility of ^{60}Co, ^{85}Sr and ^{137}Cs in a coastal sandy soil. The study focuses on a correlation between molecular-weight of dissolved humic acid and ability of the complexing with the radionuclides in liquid phase.

Dissolved humic acid was complexed with ^{60}Co and ^{85}Sr. The interaction ability of ^{60}Co was independent of molecular-weight of humic acid, while that of ^{85}Sr depended on. The mobility of ^{60}Co increased under the condition with coexistence of humic acid as well as its sorption ratio decreased. The distribution profile of molecular-weight of ^{60}Co was kept at a constant in the solution before and after the sorption experiment, due to completing the sorption and complexation equilibrium. The mobility of ^{85}Sr increased under the condition with coexistence of humic acid, in spite of the sorption ratio of ^{85}Sr was not affected by the coexistence. Such contradiction was caused by different kinetics between the batch and column methods. The sorption ability and mobility of ^{137}Cs were not affected by the coexistence of the humic acid.

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海岸砂質土壌中における^{60}Co, ^{85}Sr及び^{137}Csの移行に及ぼすフミン酸の影響

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　海岸砂質土壌中における^{60}Co, ^{85}Sr及び^{137}Csの移行性に及ぼすフミン酸錯体形成の影響を明らかにするため，溶存フミン酸の分子量とフミン酸錯体形成能との関係に着目したバッチ法収着実験並びにカラム法移行実験を行った。

　^{60}Co及び^{85}Srはフミン酸との錯体を形成した。^{60}Co錯形成能はフミン酸の分子量に依存しなかったが，^{85}Srはフミン酸の分子量に依存した。フミン酸共存条件下において，砂質土壌に対する^{60}Coの収着比は減少し，移行性は増大した。液相中^{60}Co化学種の分子量の分布は，収着平衡並びに錯化平衡の成立により，収着実験の前後において同じ傾向を示した。^{85}Srの移行性は，フミン酸共存によって収着比が影響を受けなかったのにも係わらず，フミン酸共存条件下で増大した。そのような矛盾は，バッチ法とカラム法との間での反応速度の違いから生じたものと推測された。^{137}Csの収着性と移行性はフミン酸の共存によって影響を受けなかった。

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1. INTRODUCTION

The migration of radionuclide in a shallow land is controlled by both flow characteristics of interstitial water in soil layer and physico–chemical states between radionuclide and soil. Since almost of all ionic radionuclides are interacted with soils, mobility of the radionuclides in a soil layer is retarded by the interaction. This interaction is generally expressed as a distribution coefficient, which is the ratio of the activity per unit weight of soil to the activity per unit volume of solution. It has been known the distribution coefficient is affected by environment surrounding the radionuclides, such as pH, Eh, temperature, coexistent ion, oxygen, and organic substance[1]-[5].

The involvement of dissolved organic substance in the sorption ability and mobility of the radionuclides in soil and water has been investigated by some workers[6][7]. Much of the dissolved organic substance in natural waters consists of "humic substances", which originate from the decay of organic matter in soils and waters. The resulting product "humic acid" is very stable to further decay and is of indeterminate structure, with carboxyl, methoxy, phenolic, quinone, and other functional groups, and molecular weights of under 1,000 to over 200,000[6][8]. As such humic acid has substantial chelation properties for metals, especially transition metals, it considerably affects on the sorption and migration behavior of the radionuclides in soil layer. From a geochemical point of view, it is important to know reactivity of humic acid with the radionuclides released from radioactive–waste repository.

We have studied to obtain more detailed information on the influence of humic acid complexing on the mobility of ^{60}Co, ^{85}Sr and ^{137}Cs in a coastal sandy soil. The present work focuses on a correlation between molecular–weight of the dissolved humic acid and ability of the complexing with the radionuclides in liquid phase.

2. MATERIALS AND METHODS

2.1 Soil sample

Sample used in this experiment was a coastal sandy soil collected at a site of the Tokai Research Establishment, JAERI. It was air–dried and washed with deionized water, and then sieved into a range from 250 to 350 μm in diameter. Physico–chemical properties of the sample had been reported by Tanaka et al.[5].

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2.2 Humic acid

Humic acid was purchased from the Aldrich Chemical Co. and was purified by the following procedure described by Nash et al.[9]. Solid humic acid was dissolved in 0.1 M NaOH and stirred for 24 h to digest the solid completely. The resulting solution was centrifuged at 10,000 rpm to remove insoluble humin and most of the associated inorganic solids. The solution was acidified (pH 2) with 1 M HCl to precipitate the humic acid and separate it from the acid-soluble fulvic acid fraction by centrifugation at 3,000 rpm. The solid was then washed with a mixture of 6 M HCl to dissolve remaining inorganic solids. The humic acid was then redissolved in 0.1 M NaOH and stirred for 3 d in contact with the Na^+ form of Dowex 50-X8 (60~80 mesh) cation exchange resin to remove the remaining exchangeable metal ions. The solution was again acidified with 1 M HCl to precipitate humic acid, and the solid was washed with triply distilled water to remove Cl^-. The resulting low-ash humic acid was then prepared to desired concentrations by diluting with 0.01 M $NaNO_3$.

2.3 Radionuclides

Radioactive cobalt and cesium were obtained from Radiochemical Centra, Amersham, as $^{60}CoCl_2$ and $^{137}CsCl$ solution. Radioactive strontium was purchased from New England Nuclear as $^{85}SrCl_2$ solution. A radioactive aqueous solution containing ^{60}Co, ^{85}Sr and ^{137}Cs was prepared into ca. 3.7×10^4 Bq/ml in concentration of each radionuclide, by diluting with deionized water.

2.4 Sorption experiment by batch method

After 2.5 g of the soil sample and 50 ml of the humic acid solution were transferred into 200 ml glass Erlenmeyer flasks, the radioactive solution mentioned above was added. It was kept constant at 0.01 for ion strength, 7 for pH and 25 ℃ for temperature respectively, for each particular sorption isotherm. The solutions with the soil were gently agitated on a reciprocal shaker for 7 d at 60 rpm until equilibrium was reached. Supernatant was sampled and the concentration of the humic acid and the radionuclides was analyzed. Blank tests were also carried out to examine the concentration of them in the solution before and after the mixing with the soil.

Molecular-weight of the aquatic humic acid and the radionuclides species in the solution was classified into 6 ranges by ultrafiltration technique with Millipore filters of 5,000, 10,000, 30,000, 100,000 and 300,000 in cutoff molecular weight.

Humic acid concentration in solution were measured with Shimadzu UV-240 spectrophotometer (refer to Appendix).

2.5 Migration experiment by column method

The apparatus for migration experiment is schematically illustrated in **Fig.1.** A column made of polyvinyl chloride was 2.5 cm in inner diameter and 5 cm in height and has two membrane filters of 5 μm in pore size at the top and the bottom of it. A sandy soil layer was prepared by packing the sandy soil into the column to make a bed of 5 cm thickness.

The radioactive solution of 500 ml was inflowed into the sandy soil layer from the bottom, at a flow rate of 1 ml/min. The radioactive solution was prepared to 3.7×10^3 Bq/ml for ^{60}Co, ^{85}Sr and ^{137}Cs concentrations, 0.01 for ion strength, 7 for pH, and 10 ppm-C for humic acid concentration. Effluent samples through the column were collected with a fraction collector. After the inflowing procedure, the sandy soil layer was cut into sections of 0.5 cm thick. Activity of the radionuclides in the effluent and the soil section samples was measured.

3. RESULTS AND DISCUSSION

3.1 Sorption behavior of radionuclides

The relation between sorption ratio of the radionuclides and the concentration of dissolved humic acid is shown in **Fig.2.** The sorption ratio of ^{60}Co decreased with increasing concentration of coexistent humic acid. Those of ^{85}Sr and ^{137}Cs were not affected by the coexistence of humic acid.

Figure 3(a)~(d) show the molecular-weight distribution of dissolved humic acid, and of dissolved ^{60}Co, ^{85}Sr and ^{137}Cs species, before and after the sorption experiments, under the condition with 35.0 ppm-C of humic acid. According to the blank test of humic acid, the rapid decrease of the concentration of humic acid was seen in the range of 100,000~30,000 of molecular-weight. This means that the bulk of dissolved humic acid was present in molecular-weight range from 30,000 to 100,000, as shown in **Fig.3(a).** The concentration of dissolved humic acid in each fraction and the distribution profile of molecular-weight were not varied before and after the sorption experiments. This result reveals that all fractions of humic acid are hardly sorbed by the sandy soil.

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Figure 3(b) shows the molecular-weight distribution of ^{60}Co species in the solution before and after mixing with a suspension of the sand. The lower dotted line shows the size distribution of ^{60}Co remaining in the solution after the sorption experiment. The ^{60}Co concentration in each fraction decreased after the sorption experiment, due to the sorption of ^{60}Co onto the sandy soil. The bulk of dissolved ^{60}Co was present in molecular-weight range from 30,000 to 100,000. Profile of the molecular-weight distribution of ^{60}Co was very similar to that of humic acid shown in Fig.3(a). Similar profiles of molecular-weight distribution of ^{60}Co and humic acid indicate that the dissolved humic acid contributes a forming of humic-complex of ^{60}Co and the forming ability is independent of molecular-weight of humic acid.
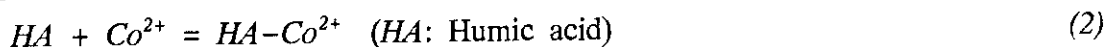
The reduction ratio of the ^{60}Co concentration in the sorption experiment to that in the blank test was nearly constant in each fraction of molecular-weight, thought the concentration of ^{60}Co in each fraction of molecular-weight decreased in the sorption experiment compared with that of ^{60}Co in the blank test. There are humic acid, humic-complex of ^{60}Co, and cationic ^{60}Co and its hydroxides in the solution. Appeared sorption of ^{60}Co is seemed to be based on a reaction with cationic ^{60}Co species, because humic acid is not sorbed onto the sandy soil as observed in Fig.3(a). The concentration of ^{60}Co in the all six fractions was constantly decreased by the sorption experiment, despite only the cationic ^{60}Co species existing in <5,000 fraction was removed from the solution. These results are explained in the following.

There are two equilibrium processes in the static sorption experiment; one is a sorption equilibrium process and the other is a complexation equilibrium process,

Sorption equilibrium:
$$Sand + Co^{2+} = Sand-Co^{2+} \tag{1}$$
Complexation equilibrium:
$$HA + Co^{2+} = HA-Co^{2+} \quad (HA: \text{Humic acid}) \tag{2}$$
In a extremely low concentration region, Eq.(1) is expressed by distribution coefficient Kd:
$$[Sand-Co^{2+}] = Kd[Co^{2+}] \tag{3}$$
Equation (2) is described by stability constant of humic-complex Kc:
$$\frac{[HA-Co^{2+}]}{[HA][Co^{2+}]^n} = Kc \tag{4}$$

When the cationic ^{60}Co is removed from the solution by Eq.(1), it will be supplied by

reverse reaction of Eq.*(2)*. In addition, kinetics of the complexation is attained more immediately than kinetics of the sorption. It is reported that the sorption process have been proceeding over 7 d in experimental period[1][4], while the complexation process is completely achieved within 2 h[10]. The Eq.*(4)* is completed during the experimental period, so the proportion of each ^{60}Co species is to be kept at a constant in the solution.

Figure 3(c) shows the molecular–weight distribution of ^{85}Sr species in the solution before and after mixing with the sandy soil. The molecular–weight distribution profile before the sorption experiment was rather similar to that of ^{60}Co and humic acid. This reveals that ^{85}Sr is also interacted with humic acid. Concentration of ^{85}Sr in each fraction was decreased by the sorption experiment, as is seen in the experiments of ^{60}Co. The reduction ratio of the ^{60}Co concentration in the sorption experiment to that in the blank test was nearly constant over the entire molecular–weigh range as seen in Fig.3(b), however, different reduction ratio of ^{85}Sr was observed between over and under 30,000 of molecular–weight in both experiments: blank test and sorption experiment of ^{85}Sr. The reduction ratio of ^{85}Sr concentration was calculated between over and under 30,000. The reduction ratio for the range over than 30,000 was 70 % and that for the range under than 30,000 was 40 %, respectively. Such results suggest that the interaction of ^{85}Sr with humic acid is dependent on the molecular–weight of dissolved humic acid.

Though ^{85}Sr also makes similar equilibriums as expressed by Eq.*(1)* and *(2)* in the solution, the complexing with humic acid is not probably stable, particularly to the complexing with that over 30,000. As soon as the cationic ^{85}Sr is removed from the solution, it might be mainly supplied again by dissociating the higher molecular–weight humic–complex. Hence the higher molecular–weight fraction is to be decreased by the sorption experiment, as seen in Fig.3(c). When such humic–complex of ^{85}Sr is easily dissociated, the ^{85}Sr sorption onto the sandy soil is to be not considerably affected by coexistent humic acid, as seen in Fig.2.

Molecular–weight distribution of ^{137}Cs species which remained in the solution before and after the sorption experiments shows a different profiles from those of ^{60}Co and ^{85}Sr, as shown in **Fig.3(d)**. The ^{137}Cs concentration in each fraction was significantly decreased by the sorption experiment. This indicates that the ^{137}Cs species did not form humic–complexes and those molecular–weights were under 5,000.

3.2 Migration behavior of radionuclides

Concentration profiles of ^{60}Co and ^{137}Cs in the effluent passed through the column

are shown in **Fig.4(a)** and **(b)**. The ^{85}Sr did not flow out through the sandy soil layer. The concentration of ^{60}Co in the effluent was increased by coexistence of 10 ppm-C humic acid, compared with the experimental results without humic acid. Whereas, that of ^{137}Cs was not affected by coexistent humic acid.

Concentration profiles of the three radionuclides in the sandy soil layer are shown in **Fig.5(a)~(c)**. The mobility of ^{60}Co and ^{85}Sr under the condition with coexistence of humic acid was larger than that under the condition with absence. On the other hand, the ^{137}Cs was not affected by the coexistence. Such tendency suggests that the complexed ^{60}Co and ^{85}Sr with humic acid move to the deeper and come out through the column. In the case of the coexistence of humic acid, concentration of ^{60}Co decreased little with increasing depth of the soil layer but that of ^{85}Sr decreased rapidly compared with the ^{60}Co. Both profiles of ^{60}Co and ^{85}Sr without humic acid look similar each other. This means that the coexistence of humic acid affects strongly on the mobility of ^{60}Co than that of ^{85}Sr.

Increase of the ^{60}Co mobility under the condition with coexistence of humic acid was agreed with a estimation from the decrease of sorption ratio with increasing humic acid concentration as seen in Fig.2. No change was seen in the mobility of ^{137}Cs between the absence and coexistence of humic acid. No change was also seen in the sorption ratio of ^{137}Cs. It was kept constant. However, the mobility of ^{85}Sr increased under the condition with coexistence of humic acid, in spite of the sorption ratio of ^{85}Sr was not affected by the coexistence. Such contradiction for ^{85}Sr might be caused by different kinetics between static state by batch method and dynamic state by column method. Reversible reactions as shown by Eq.*(3)* and *(4)* are realized in static equilibrium state completely. In the migration experiments by column method in which water flows continuously, both the sorption and complexation processes may not be completely achieved. Therefore the concentration of humic-complex increases in solution phase. The mobile complex will be considerably moved into the deeper layer accompanying with water flow.

4. CONCLUSION

Dissolved humic acid was complexed with ^{60}Co and ^{85}Sr. The mobility of ^{60}Co and ^{85}Sr increased in the sandy soil layer under the condition with coexistence of humic acid.

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The sandy soil used in the experiments has no sorbing capacity for humic acid. As some geological materials sorb humic acid very well, the mobilities of some humic-complexable radionuclides will be partly retarded by the retaining humic acid compounds on the materials. Therefore, such humic acid can be considered very effective for removing the radionuclides from solution by the formation of radionuclide–humic acid complexes at the surface of the materials.

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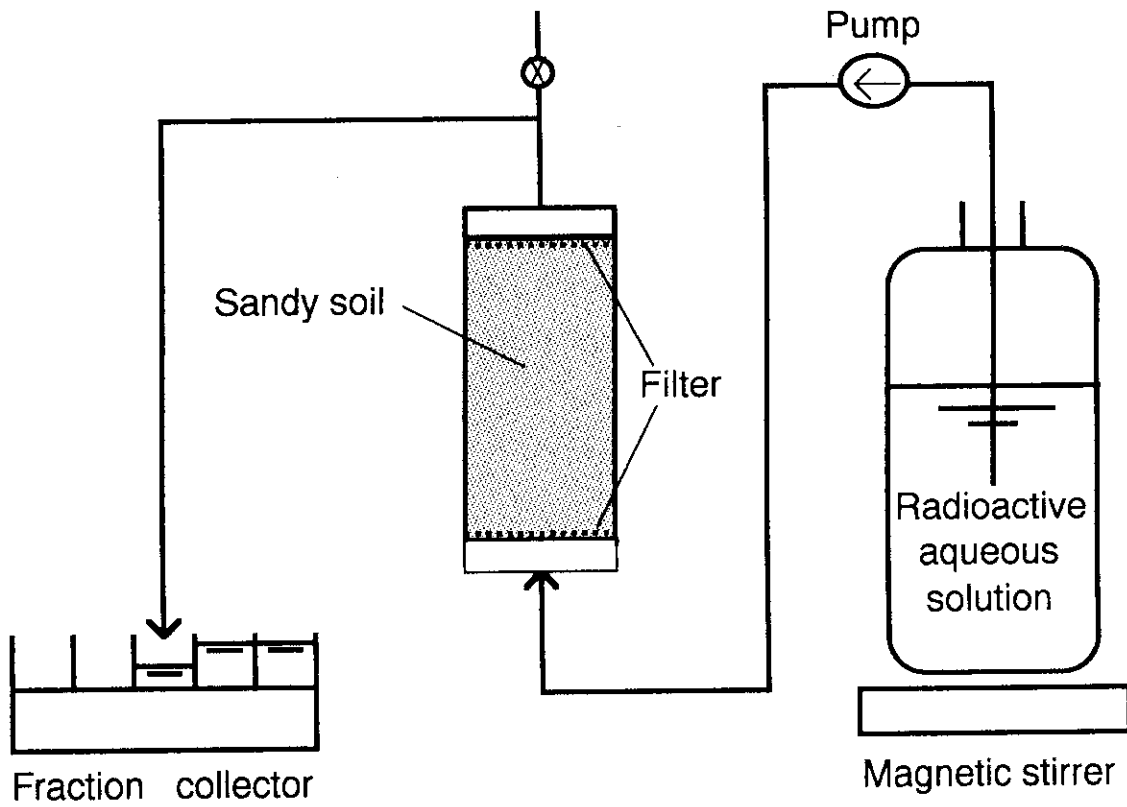(10) H.KERNDORFF and M.SCHNITZER: *Geochim.Cosmochim.Acta*, **44**, 1701 (1980).

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Fig.1 Schematic diagram for migration experiment
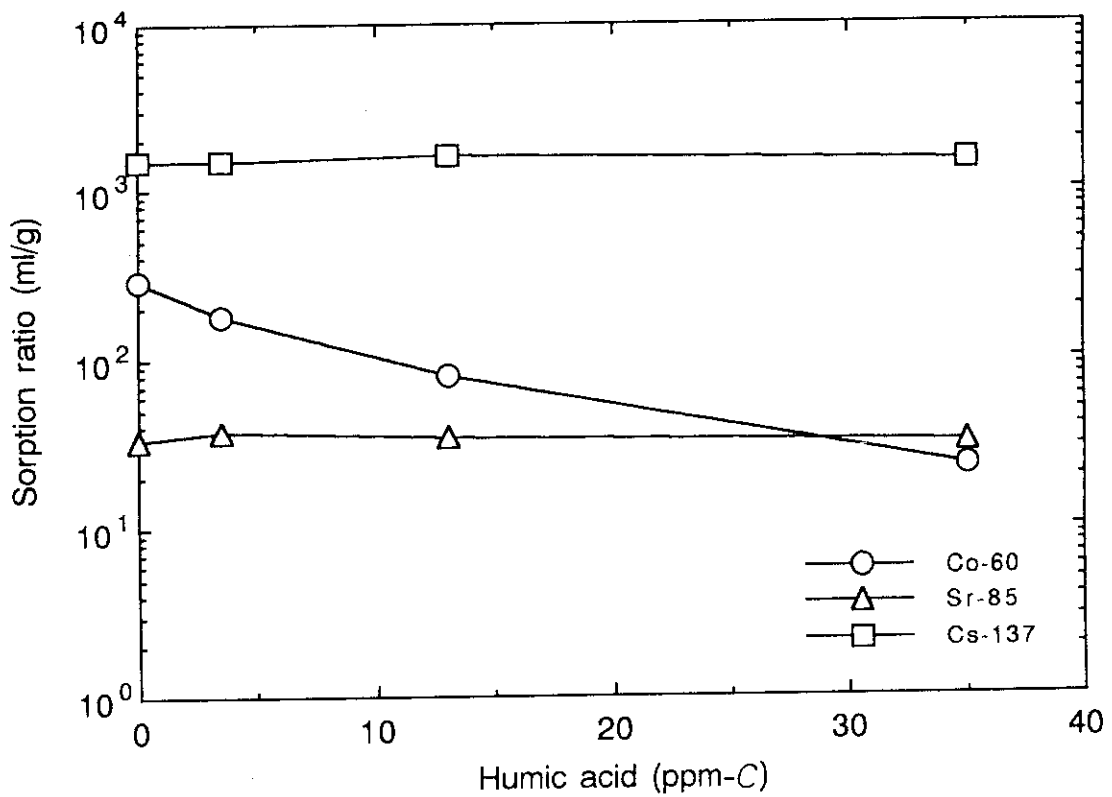
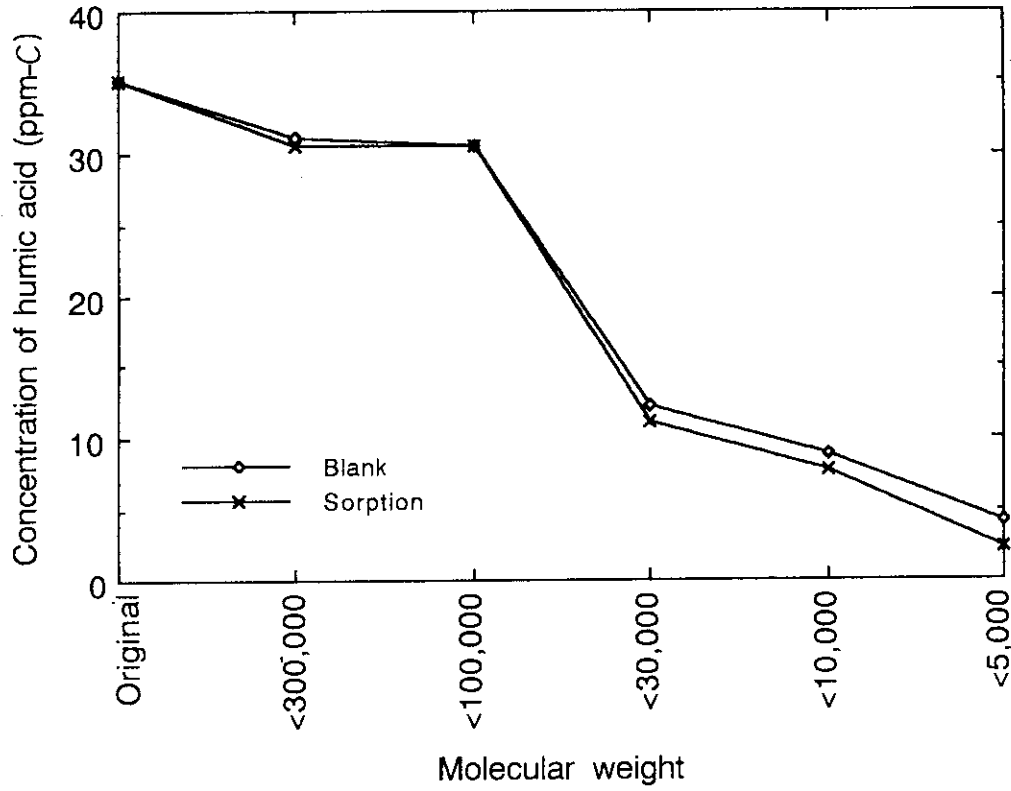Fig.2 Relation between sorption ratio and dissolved humic acid concentration

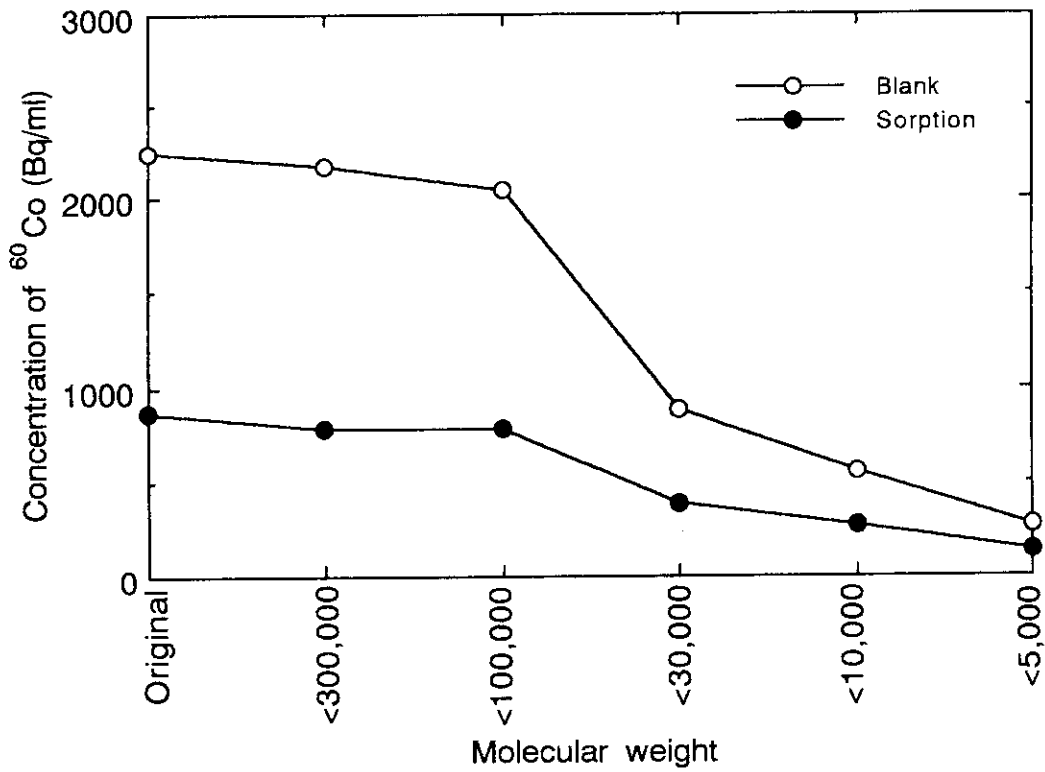Fig.3(a) Molecular–weight distribution of humic acid

Fig.3(b) Molecular–weight distribution of ^{60}Co species
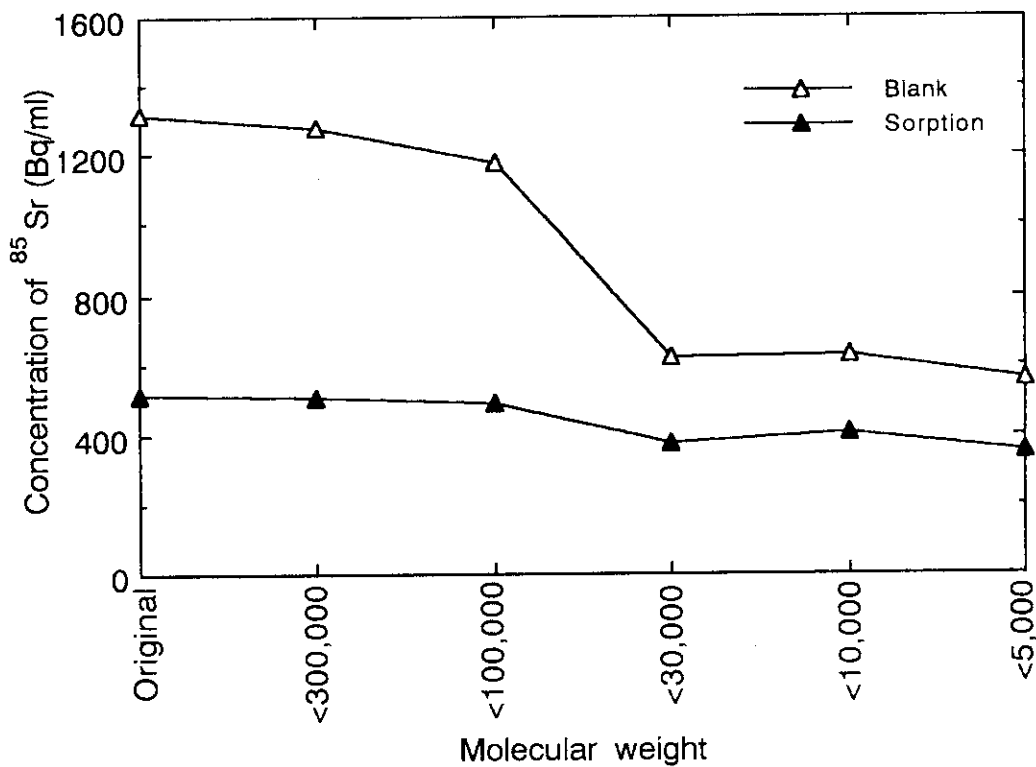
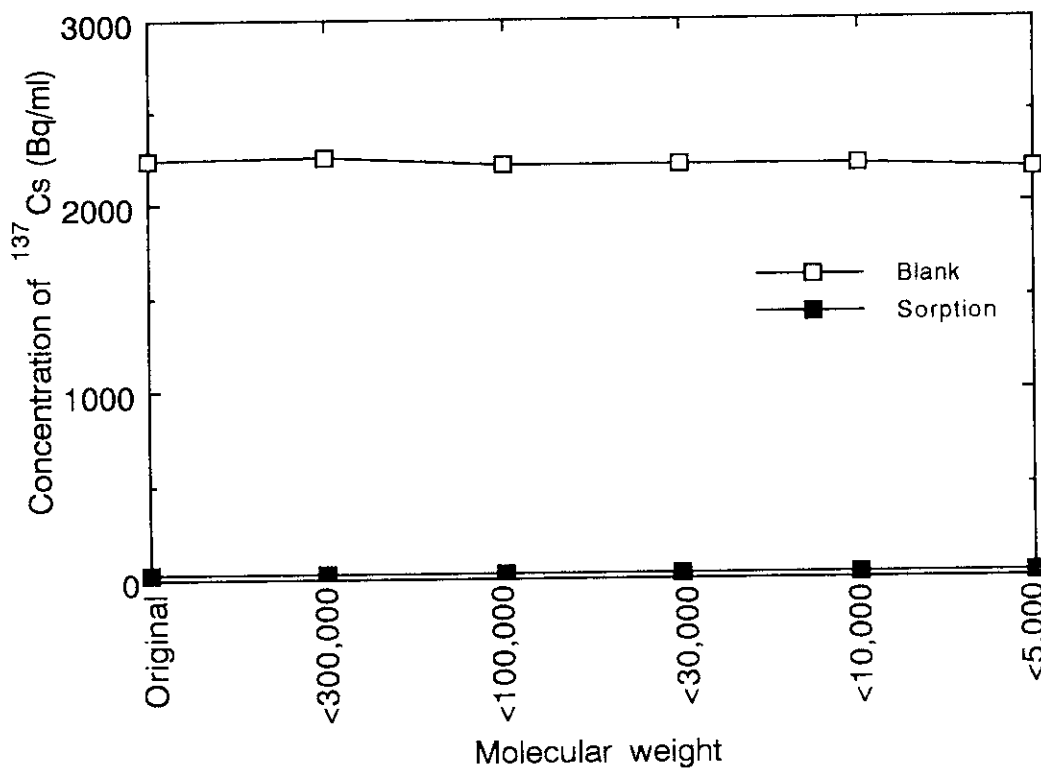Fig.3(c) Molecular-weight distribution of ^{85}Sr species

Fig.3(d) Molecular-weight distribution of ^{137}Cs species
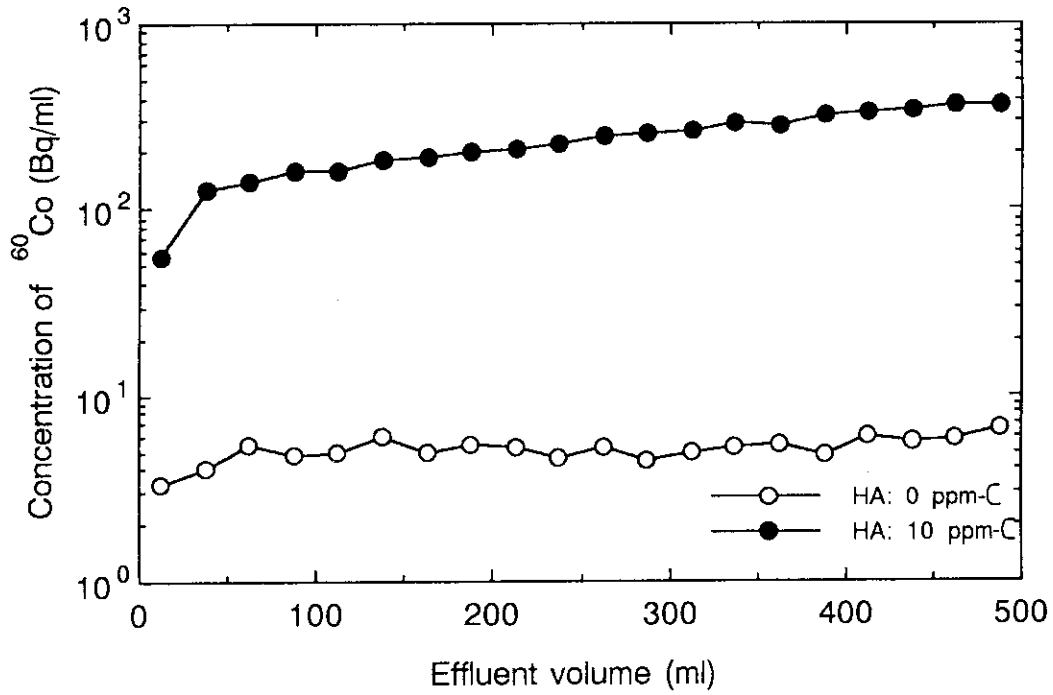
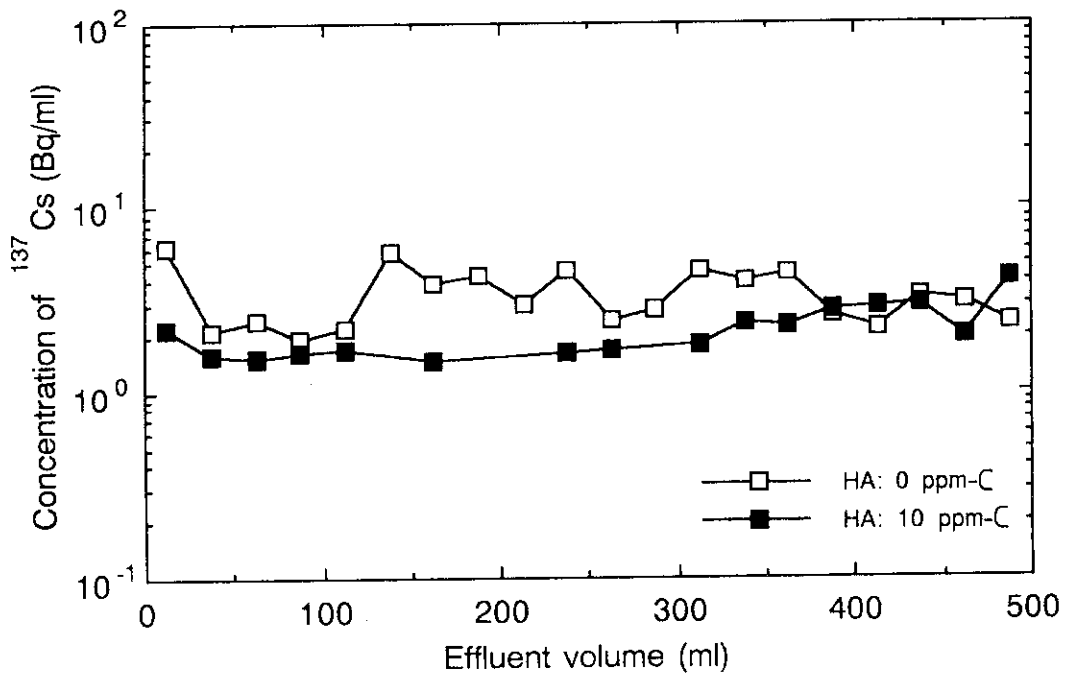Fig.4(a) Concentration profile of ^{60}Co in effluent
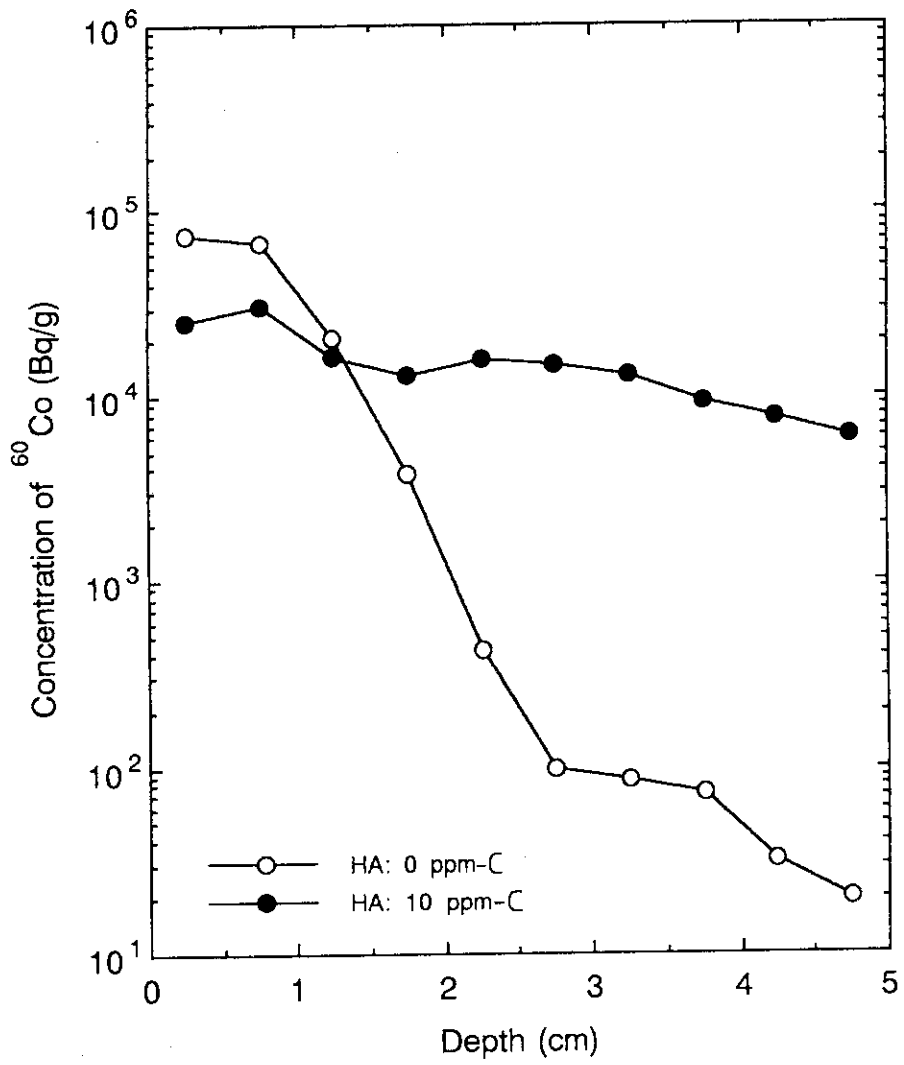

Fig.4(b) Concentration profile of ^{137}Cs in effluent

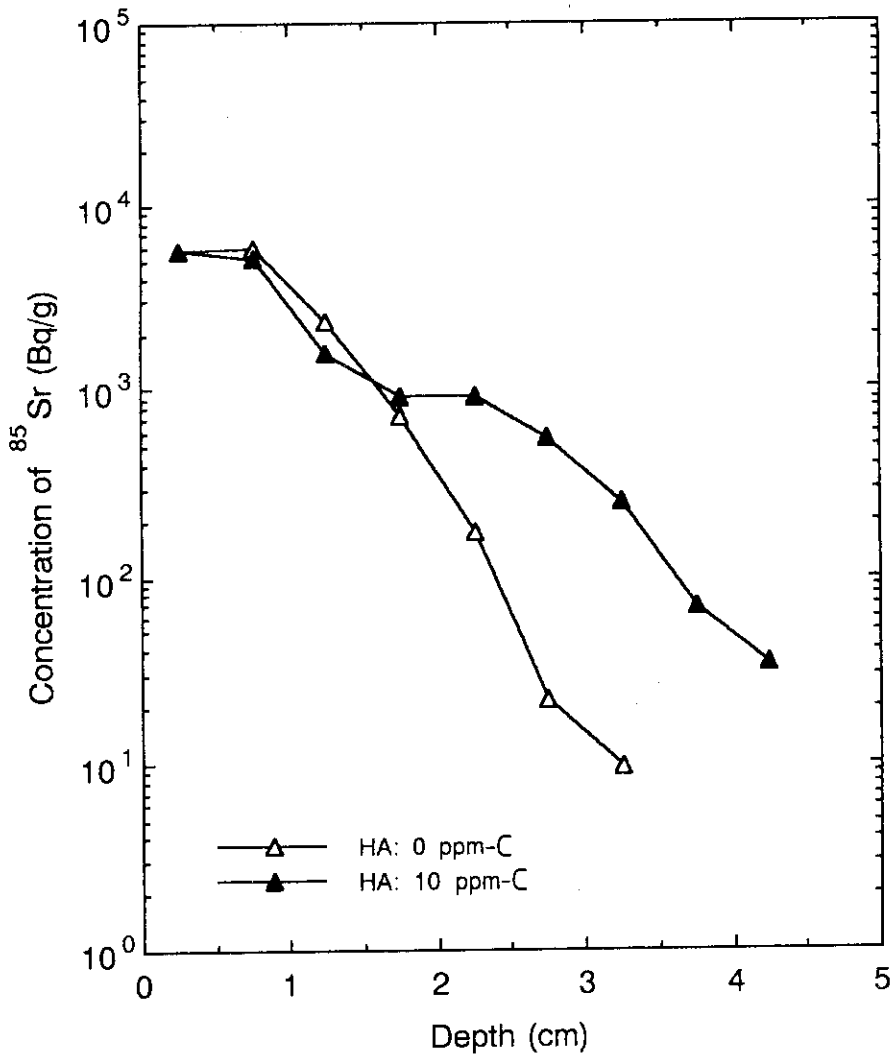Fig.5(a) Concentration profile of ^{60}Co in sandy soil layer

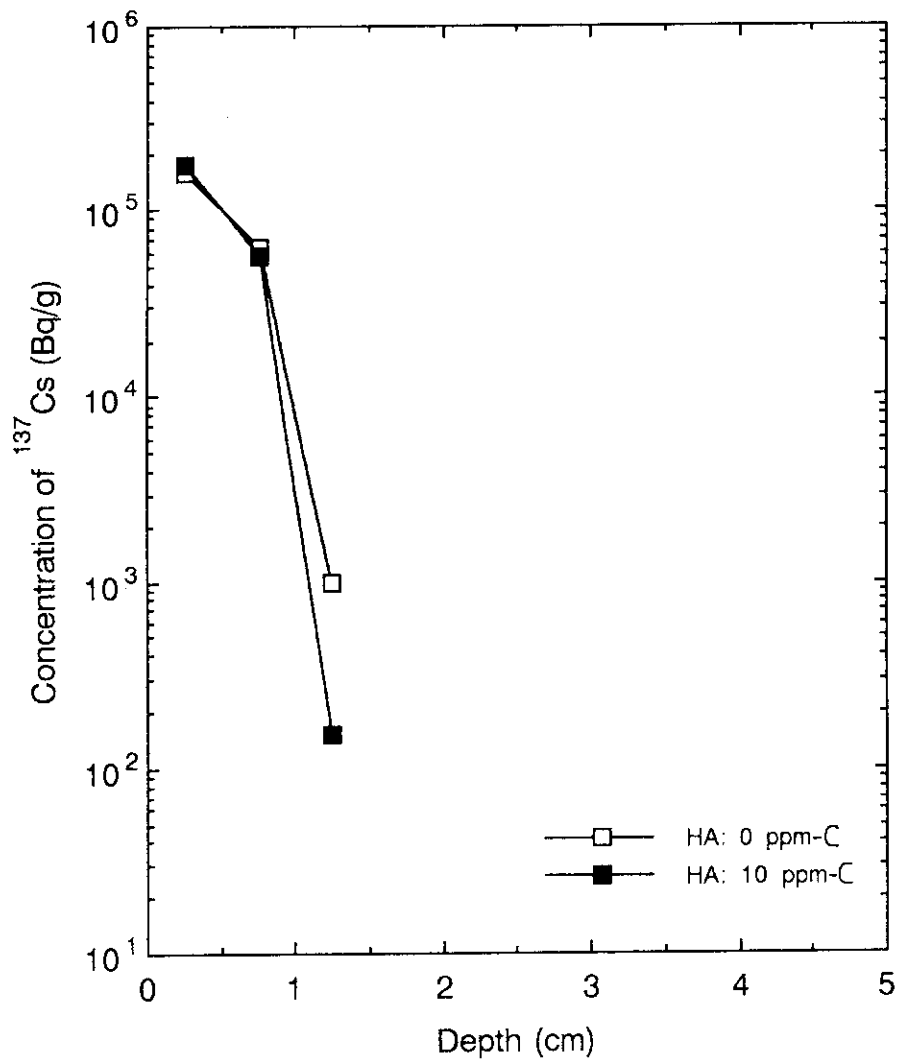Fig.5(b) Concentration profile of ^{85}Sr in sandy soil layer

Fig.5(c) Concentration profile of ^{137}Cs in sandy soil layer

APPENDIX

P.MacCarthy described as follows ("*Humic substances in soil, sediment, and water*", p.550~552, (1985), John Wiley & Sons, New York). In many instances UV–visible spectroscopy is a valuable tool in the identification of chromophobic functional groups in discrete organic molecules. But even a simple, two–component mixture may make the interpretation of a UV–visible spectrum difficult from a functional group point of view. However, UV–visible spectroscopy does have many useful applications for purposes other than determining functionality in humic substances research. Examples of these applications are in estimating the degree of humification using E_4/E_6 ratios and for determining the concentration of dissolved humic substances based on Beer's law plots for the particular substance under study.

R.L.Wershaw *et al.* pointed out about "Ultrafiltration technique as follows ("*Humic substances in soil, sediment, and water*", p.482~483, (1985), John Wiley & Sons, New York). Ultrafiltration is versatile technique which has been used to concentrate organic compounds from water, to fractionate humic substances by molecular size and to estimate molecular weights of organic matter. It has been used mostly to study aquatic humic substances although a few researchers have applied the method to soil humic material. Ultrafiltration is a method of separating macromolecules according to molecular size, by filtration under an applied hydrostatic pressure through a membrane. In theory, ultrafiltration is a rather simple process. Under hydrostatic pressure, solute molecules, within the molecular weight cutoff of the membrane, pass along with solvent through the micropores of the membrane. Even though the membranes are classified by the manufacturer according to molecular weight cutoff, it is emphasized that solute molecules are separated according to molecular size in ultrafiltration. Molecular weight data for humic substances can be estimated only by comparison of fractionation results with those obtained using suitable standards.

In the present experiment, the standard humic–acid solutions (3.5, 13.1, 21.9, 35.0, 43.8 and 65.6 ppm–C by converting into dissolved organic carbon) and the ultrafiltrated 35.0 ppm–C solutions (fractionated into <300,000, <100,000, <30,000, <10,000 and <5,000 of cutoff molecular weight) were scanned from 700 to 300 nm, for the spectral measurements. Shimadzu UV–240 recording spectrophotometer was used with 10 mm pathlength quartz cells, to record the data. The absorption spectra recorded are shown in **Fig.A1(a)** and **(b)**. **Figure A2** shows calibration curve of humic–acid concentration.

Beer's law held over the humic-acid concentration range of 3.5~65.6 ppm-C. This result shows the photometric determination is suitable for quantifying humic-acid concentration.
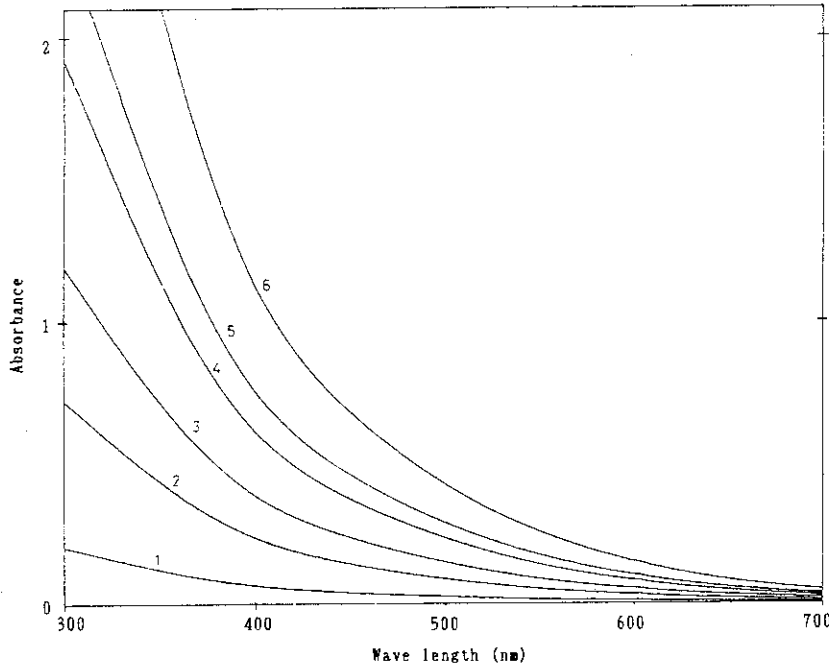

Fig.A1(a) Absorption spectrum of humic-acid; Concentration 1:3.5, 2:13.1, 3:21.9, 4:35.0, 5:43.8, 6:65.6 ppm-C
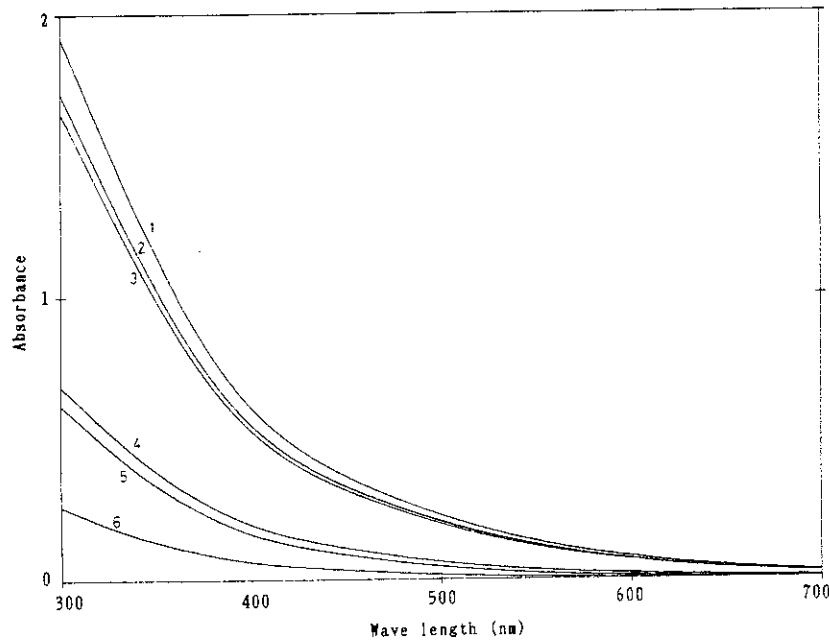

Fig.A1(b) Absorption spectrum of humic-acid; Cutoff molecular weight 1:original, 2:<300,000, 3:<100,000, 4:<30,000, 5:<10,000, 6:<5,000
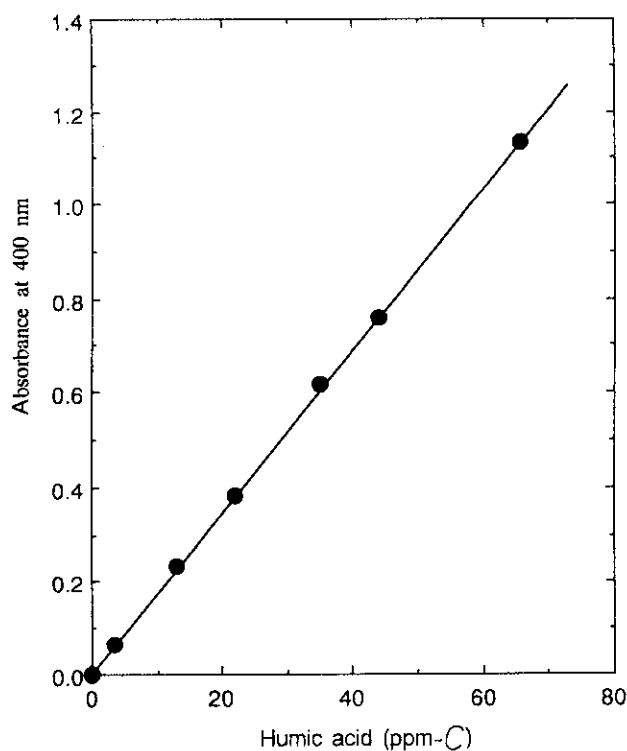
Fig.A2 Calibration curve of humic-acid concentration

The E_4/E_6 ratios (i.e., the ratio of the absorbance at 400 nm to that at 600 nm) of the spectra measured for the ultrafiltrated 35 ppm-C humic-acid solutions are given in **Table A1**.

Table A1 E_4/E_6 ratio of spectra

Cutoff molecular weight	Absorbance		E_4/E_6
	400 nm	600 nm	
Original	0.614	0.079	7.8
<300,000	0.554	0.071	7.8
<100,000	0.532	0.068	7.8
<30,000	0.198	0.019	10.4
<10,000	0.165	0.011	15.0
<5,000	0.064	0.004	16.0

The E_4/E_6 value is increased with decrease of cutoff molecular weight. The degree of humification is varied a little.